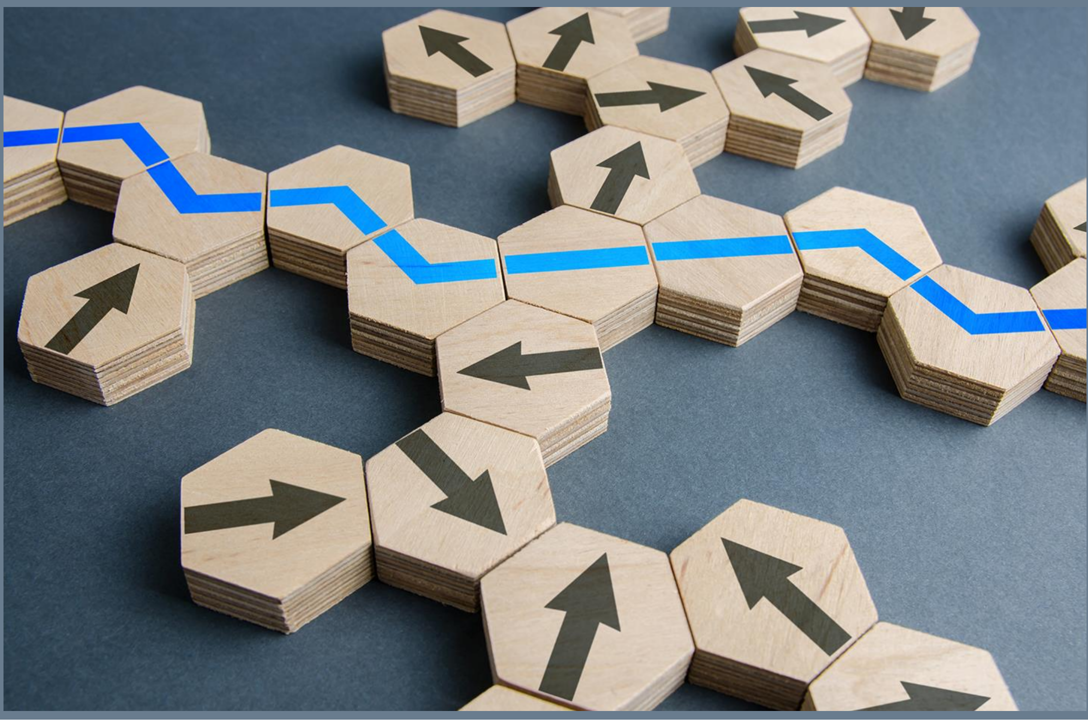

Graphene Research and Advances

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Content

Introduction

Twice a year, SIO Grafen produces a comprehensive report that provides a deeper look into the current events and trends around graphene and 2D materials. We call it Graphene Research and Advances. Here, we summarize some of the most interesting research findings that have emerged during the last few months.

In this edition, we discuss the patent landscape of graphene technology and present the latest developments from 2021. A year ago, we presented a report on patents. In this report we provide an update on what has happened since. The trends discussed are global, with a special attention to current trends in Sweden. It is interesting to note that considering the patent landscape, graphene technology appears to have entered the stabilization phase.

Graphene continues to be an interesting material for researchers, and the amount of published scientific papers is still large. However, now that more research areas are getting closer to real products, not all new and interesting discoveries are published in scientific journals. Instead, some findings are turned into new innovations in industrial settings.

Recent research articles presented in this edition highlights several interesting facts:

- Most of the existing graphene products are based on flakes of graphene. Films of graphene (made by CVD) often require a challenging transfer process. A new roll-to-roll dry transfer technique of graphene films represents an important step towards products based on films of graphene.

- Inks based on graphene can play an important role in the next generation of printed electronics.

- Graphene can be added to composites to enhance many different products. One example is to increase the performance of noise-cancelling composites.

- Membranes of graphene can be used to separate gases depending on their molecular size.

- Products with graphene can be used to tackle current and potential future pandemics.

- Graphene-based devices can be utilised to reduce the electricity consumption used to heat and cool buildings.

Patents

The last review of the patent landscape was published in a report by SIO Grafen in early December 2020. To ensure comparability of the data with the previous report, the same keywords, search string, search restrictions and Orbit Intelligence software were used. To find patents related to graphene, the search string included not only the word “graphene” but other expressions such as “two-dimensional carbon sheet”.[1] This search string was used for searches within the title, abstract, and claims of the patents and patent applications. In addition, the Swedish country code was used for geography-specific searches.[2]

Since the last published report, close to 26 000 new patent applications were made globally, counting until 1st January 2022, reaching a total count of 145 441 patent families. Although the overall number of patent families in the graphene area seems to be high, the timeline picture in Fig. 1 shows that this technology might be entering the stabilization phase or even slowing down.

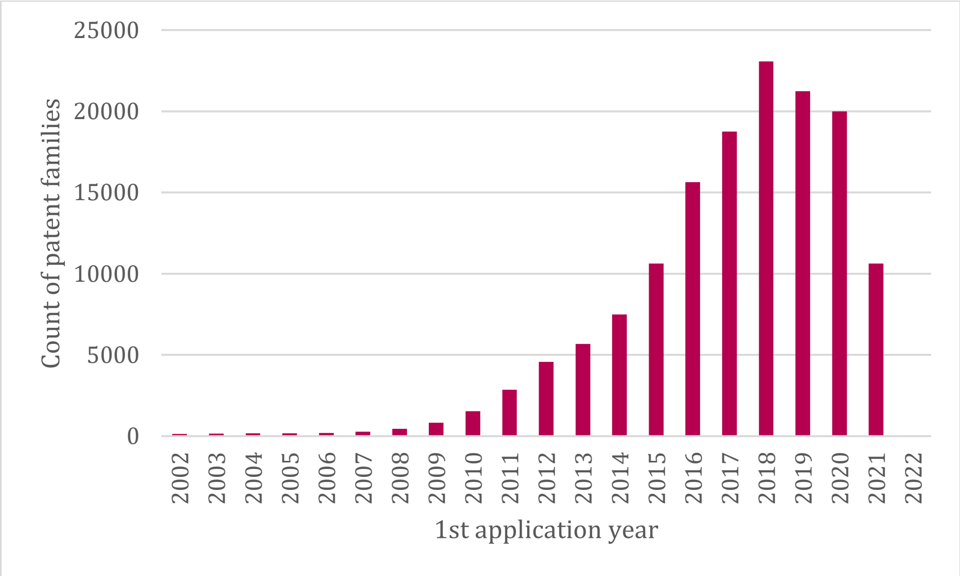

Fig. 1 Total yearly count of patent families in the last 20 years.

At this moment, it is quite hard to predict which trend will dominate as the data from the last 18 months will always be incomplete due to patenting prosecution rules.

[1] The following search string has been used: (graphen+ OR graphane OR graphyne OR graphdiyne OR graphone) OR ((single OR mono OR few OR "2"_D OR "2"_dimension?? OR two_dimension?? OR (two 2W dimension??) OR ("2" 2W dimension??) OR (one 2W atom)) 3W (layer? OR sheet? OR film? OR plate? OR ribbon? OR flake? OR flaky OR plane? OR nano_sheet? OR nano_plate? OR nano_ribbon? OR nano_flake?) 3W (carbon+ or graphit+)).

[2] The following fields were used for geographic specific searches: protection country, assignee country.

Patent applications do usually not get published until 18 months after the day of the application. That means that in the years of 2020 and 2021, the total count of patent families will increase. From all found patent families 28,2% are pending patent applications showing that it is still a heavily researched and developing technical area. Having that in mind, and considering that graphene right now is positioned on the downslope of the peak of inflated expectations on the technology hype curve, we believe that graphene is entering the much-awaited stabilization phase.

The general geographical market outlook is similar to the one reported previously. The countries with the highest count of published patent families are matching the regions where the highest number of protected patent families China, USA, and Korea are leading the race in both categories. In Europe, the most active countries are Germany, Great Britain, and France. Combining it with general knowledge of the market and research activities leads us to the conclusion that technology providers and product developers are residing in the same geographical areas. Moreover, China shouldn't only be treated as a usual cheap manufacturer, but as an active technology advancing player.

Top 10 countries where patent families are	
published	**protected**
China	China
United States	United States
South Korea	South Korea
Japan	Japan
Taiwan	Germany
Germany	Great Britain
India	Taiwan
Canada	France
Australia	India
Great Britain	Canada

In this report, we also look more closely at recent developments in Sweden. We have analyzed what is happening inside and how Swedish companies and research organizations are developing in terms of patent families output. We have also tried to identify which foreign companies are interested in seeking protection in Sweden. The data presented in the following paragraphs show the period between 1st December 2020 and 1st January 2022.

First a look at the Swedish assignees, which are the entities that have the property right to the patent. Between December 2020 and January 2022, 63 new patent families were published by a total of 43 different Swedish entities. The top 3 companies with the highest count of patent families published in that period are *Ericsson*, *Saltx Technology*, and *SKF*. Swedish assignees protect their IP related to graphene inventions according to global trends. China, USA, Germany, Japan, and Great Britain are the main geographical targets besides Sweden.

Sweden is not a top choice for patent protection in the graphene area, but there is some interest in patenting in Sweden also from companies based elsewhere. A patent database search found 173 patent families published since December 2020 that are protected in Sweden. On the top of the patent assignees list (Fig. 2) are companies of foreign origin *Hydro Quebec* with 8 patent families, *Contemporary Amperex Technology* – 4, and *Synthos* – 4. It's worth to notice that there are only 2 research institutions, the French *Commissariat à l'energie atomique et aux énergies alternatives*, and *the Norwegian University* of *Science and Technology* in the list. It is a big contrast to the global data, where 95% of the top 30 patent assignees are Asian research organizations, and the other 5% are companies from China, South Korea, and the US, plus one South Korean research institute.[3]

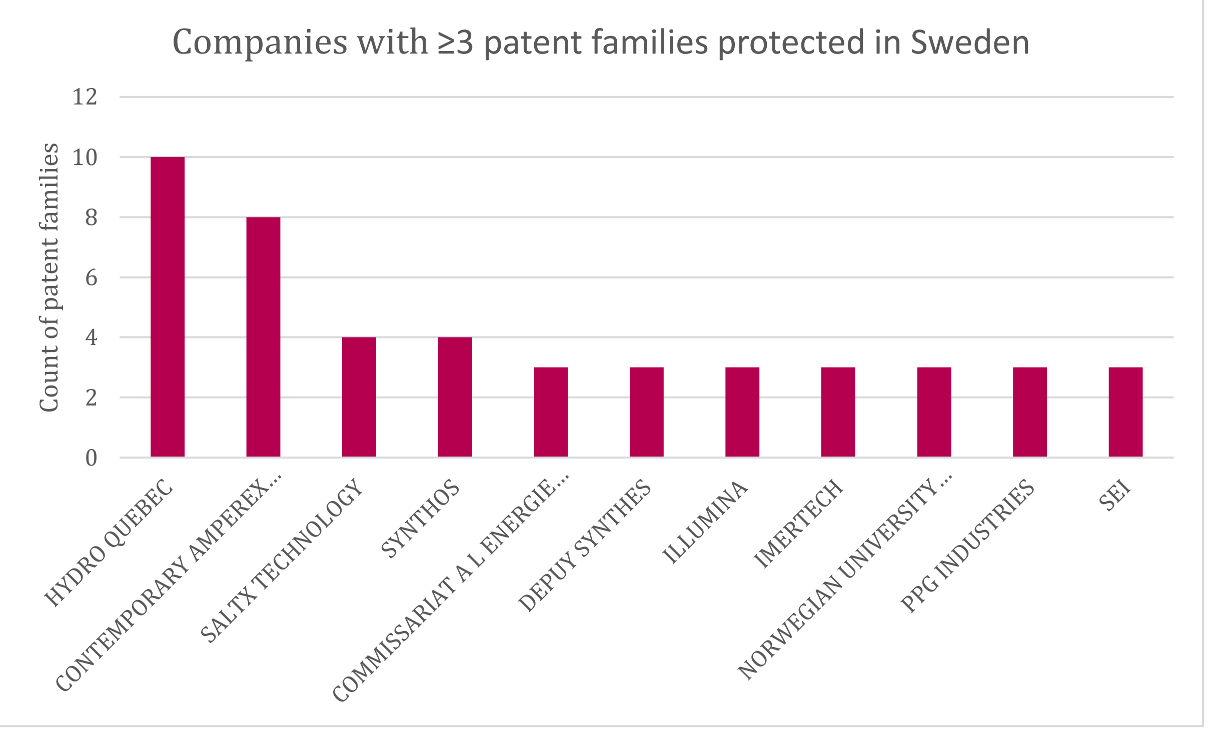

Fig. 2 List of the companies which have ≥3 patent families protected in Sweden which were published between 1st December 2020 and 1st January 2022.

[3] Full list of top 30 global patent assignees is available upon request.

State-Of-The-Art Research - Manufacturing

Roll-to-roll dry transfer of graphene

It has almost been 10 years since Sony demonstrated that large-scale production of graphene is possible with a roll-to-roll (R2R) chemical vapour deposition (CVD) method by producing a 100 meter long graphene film on a polymer substrate. However, most R2R techniques rely on wet transfer methods when transferring the graphene from the copper growth substrate to a target substrate for device manufacturing. These methods leave residues that are hard to remove and does not allow recycling of the growth substrate.

A recent report shows a new dry transfer technique that avoids chemical contamination and allows the reuse of graphene growth substrates. The sheet resistance is the lowest reported for R2R dry transferred graphene, but still rather high at 9.5 kΩ sq^{-1}. The authors produced transistors on polymer with near-zero doping level and a gate leakage current about 100 times lower than those fabricated using wet-chemical methods. This demonstrates that although there still are challenges, dry transfer methods can play an important role for high-quality and large-scale graphene applications of CVD graphene.

N. Hong *et al.*, Adv. Mater. 2106615 (2021)

State-Of-The-Art Research – Electronics

High-frequency electronics

Another recent review article is focused on microwave circuits based on graphene. Due to is high carrier mobility, graphene has great potential in this high-frequency electronics and is very promising for applications such as Radio Frequency Identification (RFID) and Near Field Communications (NFC). Graphene can be integrated on many different substrates and also be used as an add-on to other technologies, thereby giving them high-frequency possibilities (for example on flexible substrates).

However, graphene does not have any electronic band gap, which give some limitations. The technology is still young with reproducibility challenges, resulting in that fault-tolerant methodologies have to be employed. The authors summarise the current main challenges towards high performance 2D (flexible) electronics as (a) near-perfect growth, (b) layer transfer, (c) atomic layer etching, (d) low ohmic electrical contacts, (e) effective doping and (f) non-performance limiting encapsulation. When these have reached high maturity, graphene electronics will drive innovations beyond current silicon technology.

M. Saeed *et al.*, https://doi.org/10.1002/adma.202108473 (2021)

Printed electronics

The physical world is increasingly being connected to the digital world with the rapid development of Internet-of-Things (IoTs). The basics of IoTs is that a vast number of objects are being connected to the internet. This added functionality can be realised, for example by printing electronics on the objects.

Printed electronics offer several benefits over conventional electronics manufacturing. These benefits can be summarised as efficient use of materials, low manufacturing cost, minimization of energy consumption both in the manufacturing and utilization phases, reduced use of hazardous substances, and improvement of recyclability.

Researchers from Aalto University in Finland recently published a review article that summarises recent progress in printed electronics. As graphene has a high conductivity, light transmittance, mechanical strength and elasticity, it is an interesting material for printed electronics. However, the conductivity increases and the light transmittance decreases with increased amount of layers. Other materials (including other 2D materials) can thus be better suited depending on the applications. Many other materials are therefore also discussed in the paper. In the end it's not important what specific material is used, but rather the performance of the final product in comparison to the cost etc.

J. Wiklund *et al.*, J. Manuf. Mater. Process. **5**, 89 (2021)

Graphene ink

With its excellent combination of mechanical, thermal, optical, and electronic properties, graphene has attracted a lot of interest within printed electronics. However, most of these inks have used surfactants and binders to stabilise the inks. These additives then have to be removed to achieve good performance of the printed films. Some additives are also hazardous. It is therefore important to develop surfactant-free inks. An annealing step is also often required in order to produce a high-performance film.

Researchers from RISE, Uppsala University and BillerudKorsnäs have demonstrated how to make an inkjet printable starch–graphene ink and then produce highly conductive films from this ink. They produced a highly concentrated (≈3 mg/mL) inkjet printable starch–graphene ink and validated a rapid post-processing method based on photonic annealing. The process is rapid, applicable to large area processing and suitable for flexible electronics applications. The researchers believe that the simplicity and rapidness of the process have wide potential in flexible printed electronics applications.

S. Majee *et al.*, Adv. Mater. Interfaces 2101884 (2021)

State-Of-The-Art Research – Composites

Noise-reduction

Nowadays, we are exposed to noise through a significant part of our lives. It has been found that low-frequency noise especially can cause great harm as it can produce a resonance response in the human body, leading to psychological effects. Different sound-absorbing structures have therefore been created in order to mitigate this problem. Porous materials are often used as they generally have high absorption over a wide frequency range. Often, the absorption is not as good in the low frequency range.

It was recently demonstrated that graphene can be used to enhance the low-frequency absorption. A network of graphene oxide (GO) and polyvinyl alcohol (PVA) was used in combination with a porous ceramic framework. The structure was created by freeze-drying. By optimizing the suspension concentration and the amount of GO, the low frequency absorption coefficient was doubled. Additionally, the structure had a low thermal conductivity which can be important if used as for example in construction materials.

C. He *et al.*, J Am Ceram Soc. 1–12 (2022)

State-Of-The-Art Research – Coatings

Gas separation

Today, gas separation is often accomplished by separating the gases by the size of the molecule. A polymer membrane can be used, where pores in the membrane allow molecules smaller than the size of the gas molecule to pass through. For years, it has been envisioned that the next generation of this molecular sieving could be done using atomically thin two-dimensional materials with atomic scale holes. These are speculated to have superior performance as the thin membranes would allow a much higher gas flow for the same selectivity as compared to the polymeric membranes used today.

Researchers have now made experimental proof of concept studies by creating atomically small holes in graphene films. These show high selectivity and confirm a high potential in gas separation using 2D materials. However, the method used in the study is not suitable for large scale applications. The researchers are therefore now investigating alternative atomically thin materials where the holes are inherent in the material and don’t need to be artificially created one-by-one.

P. Z. Sun et al., Nature communications **12**:7170 (2021)

State-Of-The-Art Research – Biomedical Technology

Graphene to combat COVID-19

Since early 2020, the COVID-19 pandemic has affected all of us. It is obviously very important to be able to detect the virus, and there are good methods that are being used today (i.e. PCR and antigen). However, these methods entail challenges, especially when large parts of the population need to be tested.

But there are a few different ways that graphene and other 2D materials can help tackle the current and potential future pandemics. Why? Because the excellent electrical, mechanical and other functional properties of these materials can be used for the detection, protection, and continuous monitoring of infectious diseases. The high surface area and broad range of optical and electronic properties of 2D materials make them ideal for bio-sensing applications. In a recent paper, a few published examples of next generation sensors using graphene, WSe_2 and MXenes are discussed.

Graphene can also be used in e-textiles or other wearables to continuously monitor our health. This allows detection of deviations from individual's own baselines, and thereby enable more personalised healthcare.

S. Afroj *et al.*, Adv. Funct. Mater. **31**, 2107407 (2021)

Hands-free, brain-controlled devices

The ability to control devices hands-free directly from the brain has long been imagined in science fiction. This requires brain-machine interfaces that can communicate between biological electric pulses and electronic devices. Non-invasive electrodes can use electroencephalogram (EEG) analysis to interpret the brain signals. Recent advances in brain sciences have taken large steps towards realising this type of devices. However, the signal collection is challenging with detecting weak signals through the skull.

Graphene has superior biosensing capabilities. For many applications in health monitoring and neural interfaces, the flexibility of graphene is another important characteristic, whereas more mechanically stable electrodes are required in other applications. Epitaxial graphene grown on silicon carbide on silicon substrates has recently been used in a novel dry EEG electrode for brain–machine interfaces. This substrate was chosen as it allows high quality graphene on a flexible substrate if the silicon is thinner than about 50 μm, which is impossible for a pure silicon carbide substrate. The graphene devices perform better than commercial products, especially in reliability.

S. N. Faisal *et al.*, J. Neural Eng. **18**, 066035 (2021)

Bacterial sensor

Bacterial infections cause many different diseases that makes a vast amount of people suffer. In order to treat patients, reduce their suffering and stop the spread of these often infectious diseases, it is important to be able to quickly detect them. Many different diagnosis techniques are being used, but they are often quite complex, time-consuming and expensive. There is thus a need for new sensors.

Researchers at Chalmers recently demonstrated a prototype sensor based on graphene. The principle is that the electrical resistance of the graphene changes upon exposure to bacterial cells. Because graphene is so thin, it is also very sensitive. However, in many previous studies it has been a challenge that pristine graphene is not selective to specific molecules or bacteria.

The researchers at Chalmers realised that the device allowed differentiation of different bacteria based on their different growth dynamics, even though the graphene was not functionalised. The sensor is simple to fabricate and is an important step towards wider applications, for example on implants or other surfaces that needs to be kept completely free of bacteria, but where bacterial specificity is not an issue.

S. Pandit *et al.*, Sensors **21**, 8085 (2021)

State-Of-The-Art Research – Energy

Heating and cooling

A significant part of the electricity consumption is used to heat and cool buildings. A lot of this consumption could be saved by passive solar heating (absorption of solar energy) and radiation cooling (where the warm building is cooled by radiating heat into the sky). However, most material only have one of these properties, that is they can either heat or cool a building, but not switch between the two states. Electrochromic devices can change between these states by an applied current and therefore work in parts of the world that require heating and cooling at different times of the year (or day).

An electrochromic device with high performance was recently demonstrated utilizing graphene. Graphene is an ideal material as it is electrically conductive and transmits 97.7 % of the light through a very broad wavelength interval. In the heating mode, the device darkens to absorb sunlight and stop mid-infrared light (radiative heat) from escaping. In the cooling mode, on the other hand, the layer clears, exposing a mirror that reflects sunlight and allows mid-infrared light from behind the device to dissipate. The switch between the states can be done in minutes.

One of the main challenges remaining for commercial use is to be able to cycle more than the current couple dozens of times.

Y. Rao *et al.*, ACS Energy Lett. **6**, 3906–3915 (2021)

Thermal conductivity

There are many different types and sizes of graphene and it's not obvious which material to use for many applications. A recent study was focused on elucidating the role of the filler size when graphene is added to a composite in order to increase the thermal conductivity.

In contrast to previous studies, the size of the graphene flakes were chosen to be near the phonon mean free path (i.e. slightly smaller, almost equal to and and slightly larger than the mean free path of about 800 nm). This allowed the researchers to better understand the intrinsic heat conduction properties of the graphene flakes.

Unsurprisingly it was found that graphene flakes with larger lateral size results in a composite with higher thermal conductivity. The researchers were more surprised to find that also the thermal contact resistance between the composite and two contacting steel plates decreases with increasing filler size.

S. Sudhindra *et al.*, ACS Appl. Mater. Interfaces **13**, 53073–53082 (2021)

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